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Simplified Liquid-Liquid Extraction Method Analysis of Trihalomethanes in Drinking Water

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16. ABSTRACT

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A Simplified Liquid-Liquid Extraction Method for Analysis of Trihalomethanes in Drinking Water

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Abstract

A rapid, simple method for determination of trihalomethanes in water is described. The procedure involves liquid-liquid extraction by vigorous agitation of a pentane:water mixture, followed by gas chromatographic analysis of the pentane extract. Other solvents were also examined for their efficiency. The detection limit in this method is about 0.1 μg/l with a coefficient of variation ±2% through the concentration range of 14 to 160 μg/l.

Introduction

Chlorine, widely used as a disinfectant for drinking water, is known to interact with precursors (e.g., humic and fulvic acids) to yield trihalomethanes (THMs). THMs of major public health interest include chloroform, bromodichloromethane, chlorodibromomethane, and bromoform. Widespread occurrence of these compounds has been reported by the National Organics Reconnaissance Survey (1), and by the National Organics Monitoring Survey (2). Because subsequent studies (3,4) suggested that THMs can have an adverse health effect, the Environmental Protection Agency established maximum permissible levels for total trihalomethanes of 100 μg/l in potable water. It has also been proposed (5) that certain utilities be required to regularly sample and analyze their drinking water for the four designated THMs, utilizing either purge-and-trap or liquid-liquid extraction (LLE) (6).

Methods for the determination of volatile halogenated organic compounds in water that use the purge-and-trap technique as well as extraction methods have been reported by several authors (7-17). Compared to purge-and-trap methods, extraction-based procedures offer two primary advantages: (A) Analysis times can be significantly reduced. (In the authors' lab, purge and trap requires approximately 45 min/sample, while the proposed extraction procedure requires approximately 10 min/sample.) (B) Recovery and precision for all four THMs are better by LLE. These advantages are especially important in the routine analysis of a large number of samples.

The LLE procedure reported here consists of the extraction of THMs from aqueous samples into an organic solvent, followed by gas chromatographic analysis, using a Hall electrolytic conductivity detector operating in the halogen mode. The method employs methanolic THM standards and is directly applicable to aqueous samples. All four THMs can be quantified at low μg/l concentrations required by the proposed regulation when adequate precautions are taken to ensure pure solvents and high quality distilled purged water.

The procedure described was developed to avoid opening sample bottles during extraction (and so avoid loss of the more volatile components), to avoid sample transfer, and to minimize sample handling during extraction.

Experimental

Reagents. Pentane, hexane, and methyl alcohol were distilled-in-glass grade. (Burdick and Jackson). GC-grade 2,2,4-trimethyl pentane (Fisher Scientific) and methylcyclohexane (Mallinckrodt), chloroform (not stabilized), bromodichloromethane, dibromochloromethane, bromoform, and 1,1,2-trichloroethane (internal standard) (Supelco) were also used. Organic-free water was prepared by purging nitrogen gas at 100 ml/min through boiling deionized distilled water for 45 min.

Extraction vials. Vials (223745), septa (224173), and seals (224193) (Wheaton Scientific) were used. Vials, of 60-ml (60.15 ± 0.52 ml) capacity with a 20-mm mouth, were sealed with Teflon-faced silicone rubber septa, and aluminum serum bottle seals. Vials and septa were washed and rinsed with deionized distilled water and baked at 100 ± 5°C for 1 hr prior to use.

Agitator. A Model G-2 Gyrotary shaker (New Brunswick Scientific) was adapted to accommodate four horizontally mounted extraction vials.

Gas Chromatograph. A Model 560 gas chromatograph (Tracor) with a 244-cm × 2.5-mm i.d. stainless-steel column, packed with 60/80 mesh Tenax GC, and Hall electrolytic conductivity detector Model 700 was employed for analysis. Helium carrier gas was supplied at 50 ml/min, and hydrogen reaction gas at 50 ml/min. The injector was maintained at 200°C, and

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the column oven programmed from 110 to 250°C at 15°C/min. The chromatographic signal was processed via a HP 3390A integrator (Hewlett-Packard).

Standard solutions. Stock methanolic solutions of THM standards and the internal standard (IS) were prepared at μg/μl levels (0.7-2.0) by volumetric dilution. The stock solutions contained $CHCl_3$, $CHCl_2Br$, $CHClBr_2$, $CHBr_3$, and $CHCl_2CH_2Cl$ at 2.0, 2.0, 0.7, 0.7, and 1.4 μg/μl, respectively. Working standards of the four THMs and the internal standard were prepared by diluting aliquots of the stock solutions with methanol to achieve solutions of the desired concentrations.

Analytical system check. The extraction and instrument were checked daily using a standard mixture of 0.02 μg/μl each of $CHCl_3$ and $CHCl_2Br$, 0.007 μg/μl each of $CHClBr_2$ and $CHBr_3$, and 0.014 μg/μl of $CHCl_2CH_2Cl$. A given volume of this standard mixture was injected through the septum into the aqueous phase, extracted, and analyzed by the LLE method. The results were compared to a known value and if they were within ±3%, the system was performing well. If the deviation was greater than 3%, the system was recalibrated.

Liquid-liquid extraction procedure. In order to determine the precision and accuracy, as well as the detection limit of the THMs, purged distilled water was spiked with standard solution and analyzed. The 60-ml vials were completely filled with water, capped, and sealed. For samples, the vials must be filled and sealed at the sampling sites. No air bubble can be present in the vials. A 10-ml syringe was used to remove 6.0 ml of the sample from the vial and 5.0 ml of pentane was added immediately. The 1.0-ml headspace allows the solvent and sample to mix thoroughly, which is required for effective extraction. The working standards and internal standard were then injected into the sample vial, and the vial was agitated for 2 min at 300 rpm. It was found that longer agitation time did not increase the extraction efficiency. The pentane layer was allowed to separate from the water, and 3.0 μl of the pentane layer was injected into the gas chromatograph.

To determine the detection limits of the compounds, standard solutions were diluted to 1.0 pg/μl and water-spiked to give concentrations as low as 0.01 μg/l. By injecting various amounts of the standard solution or extracts, the detection limit for the THMs was determined.

Table I. Recovery of Trihalomethanes (THMs) from Water Extracted by Various Solvents (Solvent:Water Ratio = 5:54)

THM	Concentration (μg/l)	THM percent recovery			
		Pentane	Hexane	Iso-octane	Methyl cyclohexane
$CHCl_3$	40	94.7	87.6	89.0	90.2
	80	95.6	88.5	91.3	90.5
	120	95.8	88.7	92.6	92.7
	160	94.0	86.1	89.7	91.7
$CHBrCl_2$	40	96.8	89.0	91.7	90.8
	80	98.2	89.5	92.8	91.0
	120	98.5	91.6	95.0	93.7
	160	97.5	88.9	90.6	93.2
$CHBr_2Cl$	14	97.5	89.5	92.0	91.0
	28	98.9	90.0	93.8	91.5
	42	99.6	92.4	96.3	93.4
	56	98.5	91.7	92.1	92.3
$CHBr_3$	14	98.6	90.4	93.0	92.5
	28	99.5	92.0	94.5	94.5
	42	99.6	93.1	96.8	96.4
	56	99.0	92.0	93.7	95.5

Results and Discussion

Using the above procedure, recovery efficiencies for several solvents were evaluated by extracting purged water spiked with standard mixtures at four concentration levels. Peak areas that resulted from samples using the LLE procedure were compared with calibration curves obtained from the results of analysis of direct injection of standard mixtures. Pentane, hexane, methylcyclohexane, and iso-octane were used to extract different concentrations of test compounds (standards) in the purged water (Table I).

Table I shows THM recovery for 54.0-ml water samples using 5.0 ml of the indicated solvent. The sample vial volume tolerance results in an error of ±0.60%. The constant extraction efficiency over the concentration ranges 40 to 160 ($CHCl_3$ and $CHCl_2Br$) and 14 to 56 μg/l ($CHBr_2Cl$ and $CHBr_3$) are analytically favorable for all solvents tested. Several lower concentrations were examined in a preliminary study with satisfactory results, then concentrations which were of interest in an

Table II. Recovery of Trihalomethanes (THMs) from Water Extracted by Pentane at Different Water:Pentane Ratios

THM	Concentration (μg/l)	Percent recovery			
		2.5 ml	5.0 ml	7.5 ml	10.0 ml
$CHCl_3$	160	92.4	94.0	93.5	88.0
$CHCl_2Br$	160	94.7	97.5	95.6	89.0
$CHClBr_2$	56	98.0	98.5	97.5	93.8
$CHBr_3$	56	98.6	99.0	98.2	95.2

Table III. Precision of Extraction Technique As Compared to Direct Injection of Testing Standards (Pentane:Water Ratio = 5:54)

Compound	Dose level* (ng)	Coefficient of variation (%)		Extract correlation coefficient** (r)
		Testing standard	Extract	
$CHCl_3$	1.2	1.78	1.87	0.9998
	2.4	1.59	1.48	
	3.6	1.49	1.50	
	4.8	1.37	1.90	
$CHCl_2Br$	1.2	1.31	1.50	0.9998
	2.4	1.05	1.72	
	3.6	1.10	1.14	
	4.8	1.45	1.60	
$CHClBr_2$	0.42	1.41	2.40	0.9989
	0.84	1.36	1.41	
	1.26	1.40	1.44	
	1.68	2.05	2.21	
$CHBr_3$	0.42	1.43	1.37	0.9989
	0.84	1.61	1.71	
	1.26	1.16	1.22	
	1.68	1.50	1.62	

*Calculated amounts of compounds per injection
**For least squares linear regression.

Table IV. Detection Limits of Trihalomethanes (THMs) Using the LLE Procedure and the Hall Electrolytic Conductivity Detector

Compound	Standard solutions (ng)	Concentration in water (μg/l)
$CHCl_3$	0.006	0.10
$CHCl_2Br$	0.024	0.15
$CHClBr_2$	0.024	0.15
$CHBr_3$	0.03	0.20

ongoing research project were analyzed for precision and accuracy. While several solvents gave excellent recoveries, pentane was ultimately selected because of several advantages:

(A) it is readily available in pure form; (B) it is but sparingly soluble in water; (C) the distribution coefficients are adequate; (D) it separates readily from the water phase after extraction; (E) it is readily separable from the THMs by GC; (F) it is useful for the extraction of other organics in water; and (G) it gives highest recoveries of THMs.

Results of varying the volumes of pentane (2.5, 5.0, 7.5, and 10.0 ml) used for extraction of identical standard solutions are shown in Table II. Each result represents the mean of four replicate analyses. A 5-ml amount was shown to give the best results.

As shown in Table III, calibration standards were linear for all four THMs with coefficients of variation of $< 2.40\%$.

The detection limits for the LLE procedure are given in Table IV.

The simplicity, accuracy, and precision of the method have permitted an increase in the number of samples routinely analyzed in the authors' laboratory.

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